Microwave plasmas meet graphene

Dr Elena Tatarova presents the primary advantages of using microwave plasmas as a disruptive 'green' alternative for the production of high quality graphene and its derivative N-graphene at a large scale

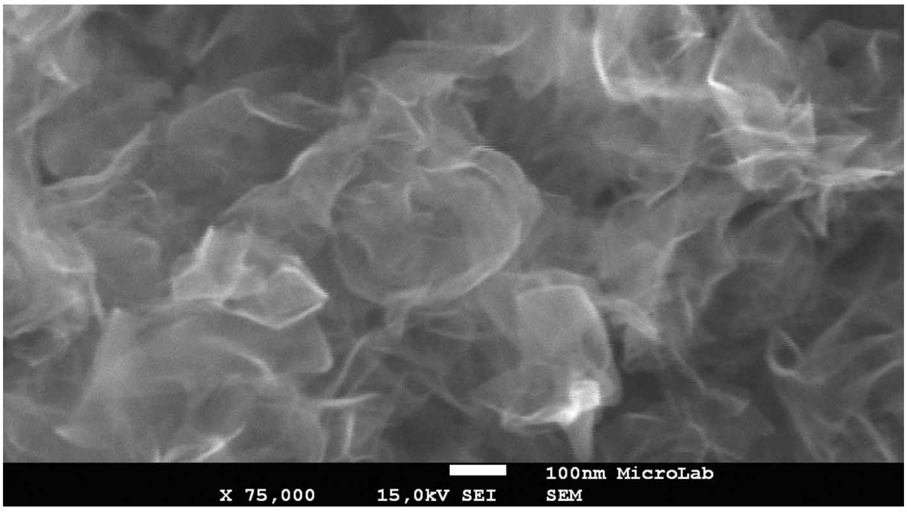
Graphene, an atom-thick hexagonal lattice of carbon atoms, exhibits a set of unique physico-chemical properties that make it highly desirable in an increasingly vast number of applications. Much of the graphene currently produced ends up being employed in scientific research. In order to boost the wider use of graphene and its derivatives and thus an enhanced utilisation of their intrinsic characteristics in practical applications, a transition to an industrial-scale fabrication process is necessary.

While a number of companies focused on the production of graphene have been created, it has been recently reported that the majority of the material made available is comprised by only 2-10% of actual graphene (see: https://www.azonano.com/article.aspx?ArticleID=4454). Furthermore, the bulk of patents has also been filled by American and Chinese research units/institutes, with the European Union falling significantly behind – with the great majority of these patents referring to either chemical vapour deposition (CVD) or exfoliation-based methods.

One of the greatest challenges in the commercialisation of graphene and its derivatives is the development of an environmentally friendly method for the production of high purity material in bulk quantities, at a low price and in a reproducible manner, with rigid control over the quality of the product. The very limited, or even absent, control over the synthesis process is one of the main limitations of conventional approaches.

Quality-demanding science

The researchers and engineers at the PEGASUS (Plasma Enabled and Graphene Allowed Synthesis of Unique nano Structures) project, which is funded by the EU FETOPEN-RIA-2017-1 H2020 programme, are determined to provide substantial evidence that microwave plasma-based technologies are a disruptive alternative route for the production of high quality graphene and its derivative N-graphene at a large scale with a controlled selection of morphologies and structural qualities via breakthrough research on plasma-enabled singular assembly pathways.



Quality/purity of the material is the main goal, with efforts currently focused on the production of high quality N-graphene free-standing flakes, as well as N-graphene/metal oxide/polymer composites and unique vertical N-graphene arrays grown on metal substrates. These are the type of nanostructures in highest demand for energy storage and conversion devices, nanocomposites, sensors, water purification, inks, lubricants, coatings etc.

The PEGASUS consortium comprises six partners from five countries (see: https://www.ipfn.tecnico.ulisboa.pt/PEGASUS/). The Institute for Plasmas and Nuclear Fusion (IPFN) is a research unit of the Instituto Superior Técnico (IST), Portugal, with a high level of expertise in plasma physics, engineering and technologies, controlled nuclear fusion, lasers and photonics and advanced computing. The research team of the Plasma Engineering Laboratory (PEL) of IPFN heads the PEGASUS project and has been carrying out complex experimental and theoretical research on microwave plasma sources and their applications over the last 15 years.

The Department for Surface Engineering and Optoelectronics (F4) at Jozef Stefan Institute, Slovenia, specialises in surface analyses and plasma technology and has a long record on nanostructure growth in plasmas, being the first to report (Dr Uros Cvelbar) the nanowire growth on solid metal surfaces during plasma exposure.

CNRS is France's most important scientific institution, with GREMI laboratories being arguably the world's largest public laboratories dedicated to the development and applications of plasmas. The Christian-Albrechts-Universitaet group in Kiel, Germany, contributes with high level of expertise in X-ray Photoelectron Spectroscopy (XPS) and

Near Edge X-ray Absorption Fine Structure spectroscopy (NEXAFS) using the BESSY II storage ring (HZB Berlin, Germany) to probe in detail the chemical, electronic and structural properties of targeted nanostructures.

The project partner from Bulgaria is the Faculty of Physics at Sofia University, which possesses a high level of expertise and experience in microwave plasmas.

C2C-NewCap LTD is a Portuguese company founded in 2014 that is developing and testing new materials for energy storage applications.

Why plasma methods?

Plasmas are high energy density environments; an assemblage of ions, electrons, atoms, and molecules that behave collectively. Plasma's remarkable potential derives from its ability to simultaneously provide dense fluxes of charged species, radicals, heat, photons and electric fields in sheath domains that can strongly influence the assembly pathways across different temporal and space scales, including the atomic. The plasma systems comprise thermal and chemical reactor functions, as well as catalytic properties. Plasma-assisted growth of nanostructures can be achieved without using catalysts due to plasma's unique ability to activate the surface, thus creating favourable conditions for nucleation and growth processes. Plasma techniques are usually environmentally clean since they do not employ primary greenhouse gas emitters.

Our graphene

In the Plasma Engineering Laboratory of IPFN, microwave-driven plasmas were successfully applied for the first time in the selective, single step, synthesis of high-quality graphene/N-graphene free-standing sheets at high-yield (~2mg/min) and at atmospheric pressure. 1g of graphene sheets as synthesised and collected by a tornado-type system (see Fig. 1).

Scanning Electron Microscopy analysis of the material revealed the characteristic curled/wavy morphology of graphene. The estimated production cost of this black, light and fluffy material is €45 per gram, including electricity, cooling and used gases, which places the process very competitively considering the price of high-quality graphene sheet products currently available.

The end-result is a high-quality product, obtained in a reproducible manner with the desired morphological, structural and functional properties: graphene free-standing sheets, collected with ~40% in the form of single atomic layers, with very low (<1%) content of oxygen and high ratio of sp^2/sp^3 carbons (~15).

Fig. 1

A new innovative plasma approach for direct synthesis of N-graphene at a high yield with control on the doping level and N bonding type is presently under development. A patent describing the process, the reactor and the system of fabrication is pending.

To this end, our key enabling technology provides a rapid, single step, cost efficient and environmentally friendly method for selective synthesis of tailored graphene/N-graphene sheets at high yield and at atmospheric pressure. It relies on a non-destructive process that does not employ toxic chemicals, heavy vacuum systems, metal catalysts or substrates, and that allows the use of carbon precursors in solid, liquid or gas state. Ethanol, biomass, 'green house' gases (CO_2, CH_4), N_2, ammonia etc. can be used as starting materials.

The main advantage of our approach is the achievement of a very high energy density in the plasma reactor in a controlled way, which allows effective control over the energy and material fluxes towards growing nanostructures at the atomic scale level via proper reactor design and tailoring of the plasma environment in a synergistic way. The ability to control the amount and localisation of energy and matter delivered from the plasma bulk to the developing nano-structures is the key to achieve the desired morphological, structural and functional properties of targeted materials, i.e., predefined outcomes.

Looking ahead

The construction of a new microwave plasma-based machine for the production of N-graphene at higher yields with an improved degree of customisation is in progress and will be delivered by the end of next year. The endeavour is deemed by Dr Bruno Gonçalves, IPFN president, as one of the most important strategic objectives of the institute and it is expected to increase the production yield by two orders of magnitude over current generation set-ups.

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IST-ID
Associação do Instituto Superior Técnico para a Investigação e Desenvolvimento

Dr Elena Tatarova
Instituto Superior Técnico, Instituto de Plasmas e Fusão Nuclear Lisboa

+351 218 419 116

e.tatarova@tecnico.ulisboa.pt
www.ipfn.tecnico.ulisboa.pt/PEGASUS/